Unusual Reductive Coupling of Alkynes and Ketones: Reactivity of Titanacycles Supported by Dimethylsilylcalix[4]arene (DMSC) Ligands

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Reaction of [(DMSC)Ti{1,2,4-$(Me_3Si)_3C_6H_3$}] (**1**) with 1 equiv of bipyridine (bpy) or 4,4′-dimethyl-2,2′-dipyridyl (dmbpy) and a slight excess of RC≡CH quantitatively produced [(DMSC)Ti(η^2-RC≡CH)(L_2)] (L_2 = bpy or dmbpy) (**5**−**16**). (DMSC)$TiPh_2$ (**17**) reacted with ≥2 equiv of bpy or dmbpy to give (DMSC)Ti$(bpy)_2$ (**18**) and (DMSC)Ti$(dmbpy)_2$ (**19**), respectively. Both ^{1}H and ^{13}C NMR data, as well as X-ray crystallography in the case of [(DMSC)Ti(η^2-HC≡CBu^t)(bpy)] (**7**), support exo-orientation of the alkyne's non-H substituent in **5**−**16**. Reaction of [(DMSC)Ti{1,2,4-$(Me_3Si)_3C_6H_3$}] (**1**) with a mixture of RC≡CH and R_2CO did not give the expected 5-oxa-1-titana-2-cyclopentene products but instead produced 2,7-dioxa-1-titana-4-cycloheptenes (**20**−**25**). The latter result may be understood in terms of the unique directing influence of the DMSC ligand.

Introduction

The use of low-valent early transition metal species in reductive couplings of unsaturated compounds is of great importance in organic synthesis and organometallic chemistry.[1] However, present knowledge of the synthesis and chemistry of well-characterized low-valent early transition metal compounds is inadequate. While some effort has been directed at studying the chemistry of low-valent early transition metal metallocenes and related organometallics,[2−13] investigations of well-characterized low-valent group 4 metal complexes supported by noncyclopentadienyl ligands are rare.[14−29] Our research group has been studying the application of calix[4]arene-derived bis(aryloxide) ligands in early transition metal chemistry.[30−33] We have synthesized

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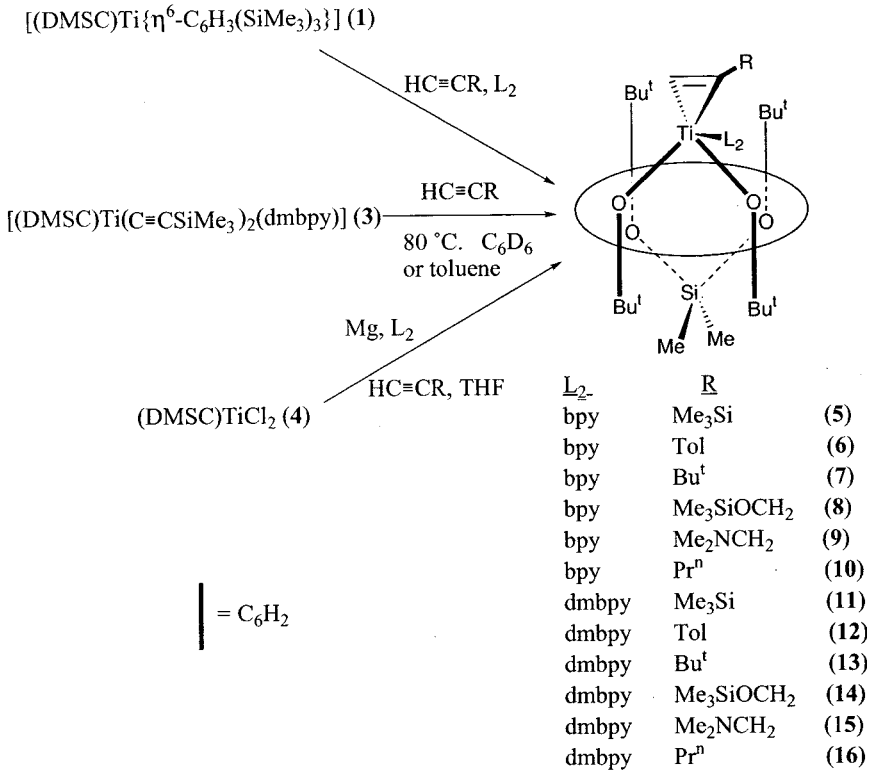
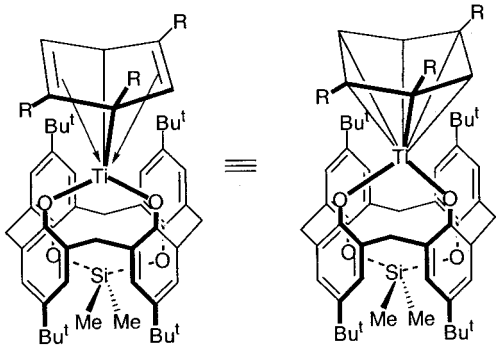
Scheme 1



[(DMSC)Ti(η^6-$C_6H_3R_3$)] complexes (DMSC = 1,2-alternate dimethylsilyl-bridged *p-tert*-butylcalix[4]arene dianion)[34] and shown that the compounds catalyze [2 + 2 + 2] cycloadditions of terminal alkynes. We showed that the high regioselectivity obtained in these cycloaddition reactions is a direct consequence of the unique steric environment imposed at Ti by the DMSC ligand.[30,31]

Well-characterized titananorbornadienes are notably rare,[17,30] and their chemistry is essentially unexplored. We have found that both [(DMSC)Ti{η^6-1,2,4-$(Me_3Si)_3C_6H_3$}] (**1**) and [(DMSC)Ti(η^6-1,3,5-$C_6H_3Bu^t_3$] (**2**) are



1, R = $SiMe_3$

excellent (DMSC)Ti(II) synthons. We saw advantage in employing the compounds to further explore the chemistry of the (DMSC)Ti(II) fragment. In this report, we describe the synthesis and characterization of titanium η^2-alkyne complexes supported by the DMSC ligand. The unusual formation of 2,7-dioxa-1-titana-4-cycloheptenes from the reductive coupling of an alkyne and two ketone molecules is analyzed on the basis of the structural properties of DMSC-based titanium η^2-alkyne complexes and the reactivity of DMSC-based titanacycles.

(34) For the synthesis of $(DMSC)H_2$, see: Fan, M.; Zhang, H.; Lattman, M. *Organometallics* **1996**, *15*, 5216.

Results and Discussion

Titanium−η^2-Alkyne Complexes. Addition of the titananorbornadiene (η^6-arene) complex [(DMSC)Ti-{1,2,4-$(Me_3Si)_3C_6H_3$}] (**1**) to hydrocarbon solutions containing 1 equiv of bipyridine (bpy) or 4,4′-dimethyl-2,2′-dipyridyl (dmbpy) and a slight excess of alkyne quantitatively produced [(DMSC)Ti(η^2-alkyne)(L_2)] (L_2 = bpy or dmbpy) (**5**−**16**) (Scheme 1). Heating a C_6D_6 or toluene solution of [(DMSC)Ti($C{\equiv}CSiMe_3$)$_2$(dmbpy)] (**3**)[31] with an alkyne will also yield the corresponding titanium−η^2-alkyne compound. For example, reaction of **3** with $Me_3SiC{\equiv}CH$ resulted in near-quantitative formation of **11**, observed along with $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ by ^{1}H NMR.[35] **11** could also be prepared via reduction in THF of $(DMSC)TiCl_2$ (**4**) with Mg in the presence of dmbpy and $Me_3SiC{\equiv}CH$ (Scheme 1). However, as a general approach to Ti−η^2-alkyne compounds, the latter method is plagued with low yield and poor reproducibility. Moreover, the desired products are often contaminated with impurities. **5**−**16** were isolated as air- and moisture-sensitive brown (or brown-purple) solids. In solution, they range in color from dark blue-green to dark purple. Their decomposition in air is noticeably slower than for other (DMSC)Ti-based complexes with Ti−C bonds,

(35) When a C_6D_6 solution of **3** was heated in the absence of an alkyne, although the elimination of $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ occurred (NMR), the Ti-containing product(s) of this reaction are presumably paramagnetic since no other significant peaks could be observed in the ^{1}H NMR spectrum. Also, the resulting deep-blue solution did not react with added alkyne.

Table 1. Crystal Data and Experimental Details for Complexes 7 and 20

	7	20
empirical formula	$C_{67}H_{88}N_2O_4SiTi$	$C_{87}H_{111}O_{7.50}Si_2Ti$
fw	1061.38	1380.84
cryst syste	triclinic	monoclinic
space group	$P\bar{1}$	$C1_2/c_1$
a (Å)	14.542(3)	49.195(5)
b (Å)	14.587(4)	13.934(2)
c (Å)	15.064(4)	23.577(3)
α (deg)	87.950(3)	90
β (deg)	75.420(3)	99.77(1)
γ (deg)	89.670(3)	90
V (Å^3)	3090.5(13)	15927(3)
Z	2	8
D_{calcd}(g/cm^3)	1.141	1.152
F(000)	1144.00	5944
λ(Mo, Kα), Å	0.71073	0.71073
μ (mm^{-1})	0.205	0.191
data collection range, 2θ (deg)	4.40−45.00	3.62−50.00
no. reflns collected	13 094	26 360
no. unique reflns	7865 [R(int) = 0.0971]	14024 [R(int) = 0.033]
goodness-of-fit on F^2	1.229	1.18
final R indices [$I>2\sigma(I)$]	R1 = 0.1559	R1 = 0.067
R indices (all data)	R1 = 0.1966	R1 = 0.091
largest peak (e$^-$/Å^3)	0.563	0.57
min. peak (e$^-$/Å^3)	−0.634	−0.72

most likely reflecting a stabilizing influence of the bpy (dmbpy) ligand due to steric saturation of the coordination sphere. Consequently, whereas solid samples of **1** and **2** decompose on contact with air, complete decomposition of solid samples of **7** and **9** occurs only after several hours in air. All of the compounds are insoluble in pentane and moderately soluble in THF and aromatic solvents. In C_6D_6, the compounds are thermally stable and did not undergo any observable decomposition at 22 °C for several hours.

An X-ray diffraction study was carried out on a multiply twinned crystal of [(DMSC)Ti(η^2-HC≡CBu^t)(bpy)] (**7**). The crystallographic data for **7** are listed in Table 1. Unfortunately, poor crystal quality limits the accuracy of geometrical parameters. Nevertheless, the connectivity is unambiguous and bond lengths and angles are within expected ranges (Figure 1). The DMSC ligand adopts 1,2-alternate conformation and the geometry around the Ti center can be described as

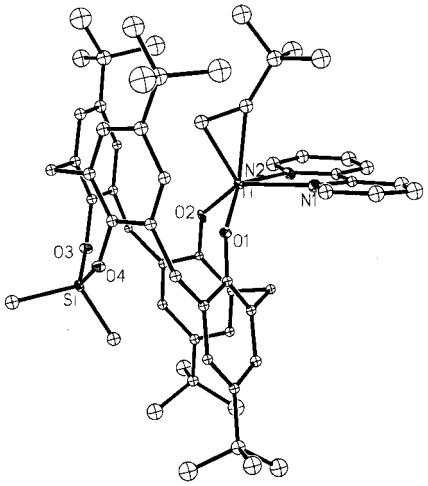


Figure 1. Molecular structure of **7** (30% probability ellipsoids).

distorted tetragonal pyramidal. The O_2N_2 set from the DMSC ligand and bipyridine occupies the basal sites, and the alkyne ligand occupies the apical site. This structure is similar to that reported for (Oep)Ti(η^2-PhC≡CPh) (Oep = octaethylporphyrin), where the N_4 set of the porphyrin occupies the four basal sites.[20] The alkyne in **7** is coordinated so as to orient the *tert*-butyl substituent out of the calixarene cavity. An exo-orientation of the Bu^t group is apparently preferred since endo-orientation (inside the calixarene cavity) would result in unfavorable steric interactions.

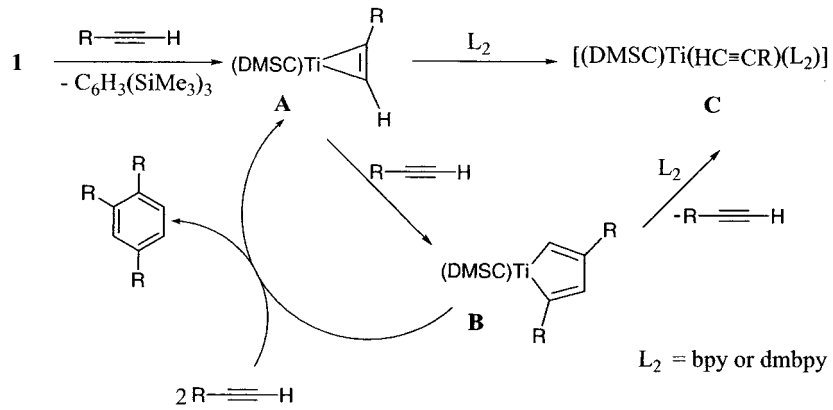
Compounds **5**−**16** are diamagnetic and give sharp solution NMR spectra. The solution NMR data are consistent with the existence of the DMSC ligand in 1,2-alternate conformation and show that the compounds are C_s-symmetric in solution. Notably, the DMSC ligands of **5**−**16** have very similar ^{1}H NMR features: their *exo*-SiMe groups have nearly identical chemical shifts, as do their *endo*-SiMe groups. The *anti*-CH_2 protons show as an AB pair of doublets (2H each, J = 17 Hz). Each of the two different *syn*-CH_2 groups shows as a pair of doublets (J = 14 Hz for one pair, J = 13 Hz for the other pair).[36] Only the chemical shifts of *syn*-CH_2 protons with J = 13 Hz show observable dependence on the nature of the alkyne substituent. The pair of doublets for these protons are shifted to high field relative to all other CH_2 protons (see Experimental Section). Both the shift to high field and the dependence of their chemical shifts on the alkyne suggest that this is the CH_2 group that is located under the bpy (or dmbpy) rings (Figure 1). The doublet at higher field likely corresponds to the hydrogen pointing toward the bpy ring system, since it would be subject to greater ring current effect. It is important to note that the largest high-field shift of these protons is observed for complexes of Me_3SiC≡CH and Bu^{t}C≡CH (**5**, **7**, **11**, and **13**). Presumably, steric interaction with the bulky $SiMe_3$ or Bu^t group forces the bipyridine moiety closer to the *syn*-CH_2 group. The close similarity of the ^{1}H NMR data for the DMSC ligand of **5**−**16** indicates that the *endo*-environment is virtually identical in all of the compounds. It is therefore reasonable to conclude that the alkyne's non-H substituent is oriented out of the calixarene cavity in all of the complexes. An exo-orientation of the alkyne's non-H substituent is consistent with the high regioselectivity and the proposed mechanism of alkyne cyclotrimerization catalyzed by (DMSC)-based Ti compounds.[30,31]

The NMR data of **5**−**16** are consistent with assignment of the alkyne ligands as 4e donors. In the ^{1}H NMR spectra of **5**−**16**, the acetylenic proton of RC≡CH resonates in the 7.2−8.2 ppm region.[37] ^{13}C NMR spectra were obtained for selected compounds: two signals were observed for the acetylenic carbons at δ 200.5 and 190.2 ppm for **7**, 208.4 and 190.8 ppm for **11**, and 189.5 and 186.3 ppm for **12**. These chemical shift values are at the high-field end of the range typical for 4e-donor alkynes,[38,39] perhaps reflecting the ring current effect of the calixarene ligand and/or the bipyridine moiety.

(36) *anti*-CH_2 refers to a methylene unit bonded to phenol rings that are oriented such that the oxygen atoms point in opposite directions, and vice versa for *syn*-CH_2.[32]

(37) These hydrogens are located inside the calixarene cavity and probably experience the ring current effect of the ligand's aromatic rings. Such an effect in the DMSC-based compounds typically causes a high-field shift of 1−1.5 ppm.

Scheme 2



Consistent with a titanacyclopropene structure, protolysis of **12** with Pr^{i}OH produced 4-methylstyrene. The protonation was slow at 22 °C but was complete in 10 min at 80 °C. Interestingly, the reaction between **12** and benzaldehyde occurred with release of alkyne, forming a mixture of Ti-containing products.[40] In the latter reaction, **12** may be viewed as behaving as a Ti(II)−alkyne complex. However, release of an alkyne can also be viewed as reductive elimination from a titanacyclopropene. Unambiguous characterization of the oxidation state of the titanium center in **5**−**16** must await further structural and electrochemical investigation.

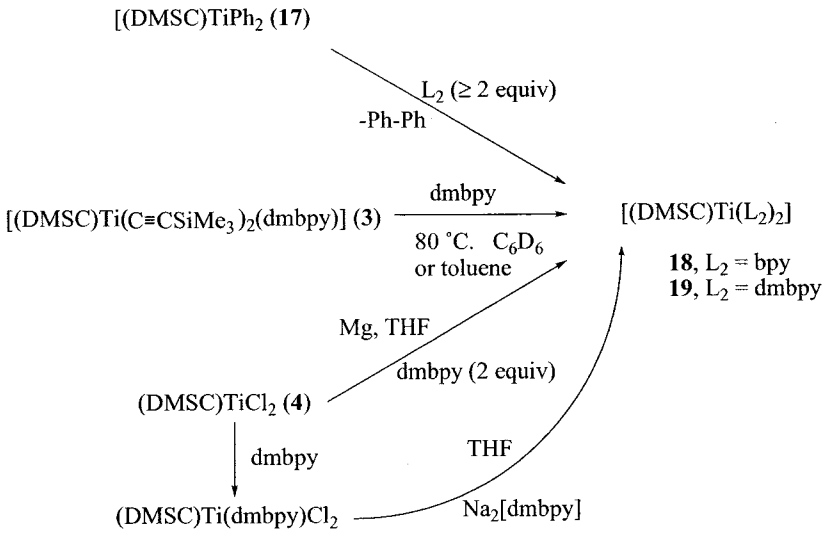
The mechanism of the formation of **5**−**16** evidently depends on the starting material. With [(DMSC)Ti(C≡CSiMe$_3$)$_2$(dmbpy)] (**3**) or [(DMSC)Ti(dmbpy)Cl$_2$] (derived from **4**) as starting material, the dmbpy ligand is bonded to Ti prior to coordination of the alkyne. Thus, the formation of a titanium η^2-alkyne complex likely occurs via (DMSC)Ti(dmbpy) species, which is trapped by the alkyne.[41] With [(DMSC)Ti(1,2,4-(Me$_3$Si)$_3$C$_6$H$_3$)] (**1**), the rate-limiting step in the formation of **5**−**16** is very likely the displacement of the η^6-C$_6$H$_3$(SiMe$_3$)$_3$ ligand from Ti by alkyne. We have already shown arene displacement to be rate-limiting for [(DMSC)Ti{1,2,4-(Me$_3$Si)$_3$C$_6$H$_3$}]-catalyzed cyclotrimerization of Me$_3$SiC≡CH (and apparently other alkynes). Moreover, we showed that this step proceeds via an associative mechanism.[30] The formation of **5**−**16** can be conveniently monitored by ^{1}H NMR. Besides free alkyne and **1**, alkyne cyclotrimerization products and the appropriate [(DMSC)Ti(alkyne)-(L$_2$)] complex are the only species observed in solution. In light of the time scale of the reaction, direct reaction between bpy (dmbpy) and **1** can be disregarded since bipyridines react very slowly with **1** ($t_{1/2} \approx 7$ days). The formation of **5**−**16** may thus be viewed to occur via L$_2$-interception of (DMSC)Ti(alkyne) species. A probable reaction sequence is illustrated in Scheme 2. The putative η^2-alkyne species **A** can be trapped by a bpy (dmbpy) molecule to give **C** directly. Otherwise **A** can react with an equivalent of RC≡CH to give **B**. Given the propensity of five-membered titanacycles toward fragmentation,[7,23,26,42,43] it is likely that coordination of bpy (dmbpy) to **B** will lead to the formation of **C** with loss of an alkyne molecule. The reaction of **B** with an alkyne molecule will of course generate Ti−η^6-arene species, from which the arene may be released. This would account for the observed cyclotrimerization products.

[(DMSC)Ti(L$_2$)$_2$] Complexes. The reaction between (DMSC)TiPh$_2$ (**17**) and two or more equivalents of bipyridine or 4,4′-dimethyl-2,2′-dipyridyl results in near quantitative formation of (DMSC)Ti(bpy)$_2$ (**18**) and (DMSC)Ti(dmbpy)$_2$ (**19**), respectively (Scheme 3). ^{1}H NMR also revealed near quantitative formation of biphenyl in the reactions. Alternative routes to **19** are also depicted in Scheme 3. It is worth mentioning that reaction of **17** with less than 2 equiv of bpy (dmbpy) does not yield the putative intermediate to **18** (**19**), (DMSC)Ti(L$_2$)Ph$_2$ (L$_2$ = bpy or dmbpy). Instead, **18** (**19**) was the only product observed, with the appropriate molar amount of **17** remaining. This suggests that, unlike the case of **3**, elimination of biphenyl from (DMSC)Ti(L$_2$)Ph$_2$ is faster than coordination of a bipyridine molecule to **17**. The more facile reductive elimination of biphenyl may be a result of greater steric congestion in (DMSC)Ti(L$_2$)Ph$_2$ versus (DMSC)Ti(L$_2$)-(C≡CSiMe$_3$)$_2$. Bipyridine-induced reductive elimination has previously been observed by Rothwell and coworkers.[44] Rothwell isolated the related deep blue-green complex (ArO)$_2$Ti(bpy)$_2$ (Ar = 2,6-Pr$^i_2$C$_6$H$_3$) and tentatively assigned the oxidation state of Ti as +2 based on electrochemical studies.[44] **18** and **19** were isolated as deep dark-blue, air- and moisture-sensitive solids. Spectroscopic and microanalysis data confirmed the formulation given for **18** and **19**. Solution NMR studies show that the compounds are C_s-symmetric at 22 °C and that the DMSC ligand adopts 1,2-alternate conformation. However, the NMR data does not allow for the geometry about Ti to be unequivocally established. Attempts to grow single crystals suitable for an X-ray diffraction study have so far been unsuccessful.

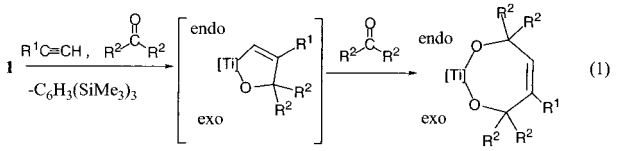
Alkyne and Ketone Coupling Reactions. Coupling of alkynes with ketones or aldehydes by a low-valent transition metal to produce allylic alcohols (upon hy-

(38) Rosenthal, U.; Oehme, G.; Burlakov, V. V.; Petrovskii, P. V.; Shur, V. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *391*, 119.
(39) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.
(40) The mixture of products is same as that formed in the reaction of [(DMSC)Ti(1,2,4-(Me$_3$Si)$_3$C$_6$H$_3$)] (**1**) and benzaldehyde.[33]
(41) Reaction of alkyne with (DMSC)Ti(dmbpy) must apparently be fast enough to prevent competing decomposition of (DMSC)Ti(dmbpy) to unidentified paramagnetic species which do not react with alkynes.[35] Otherwise prior coordination of alkyne to Ti occurs under these conditions.
(42) Grubbs, R. H.; Miyashita, A. *J. Chem. Soc., Chem. Commun.* **1977**, 864.
(43) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 1300.
(44) Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1987**, *109*, 4720.

Scheme 3



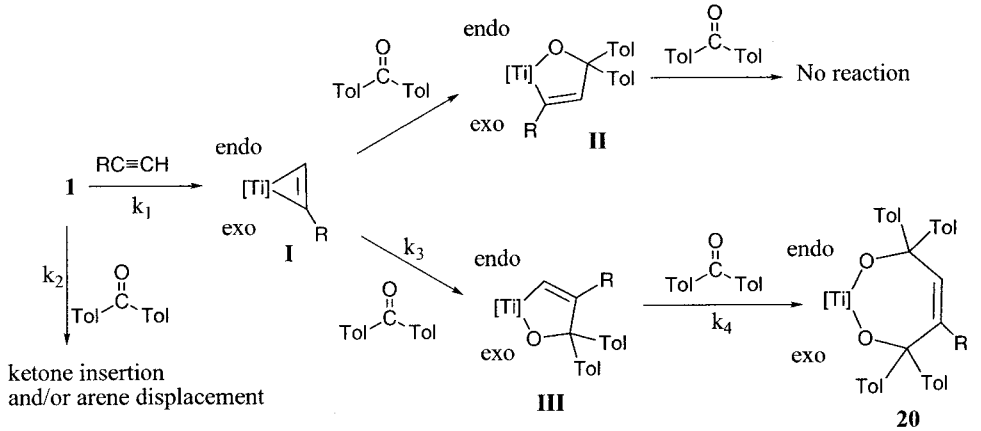
drolysis) is an attractive synthetic method.[1a,k−s] As discussed above, the formation of **5**−**16** may be considered to proceed by L_2-interception of (DMSC)Ti(η^2-alkyne) species, generated from **1**. We envisioned that such species should be similarly intercepted by ketones and that the directing influence of the DMSC ligand should promote regiospecific coupling of the substituted carbon of a terminal alkyne with the ketone. In fact, our expectations were realized (vide infra), but 2,7-dioxa-1-titana-4-cycloheptenes (**20**−**25**) were produced



instead of the expected 5-oxa-1-titana-2-cyclopentene products (eq 1). A typical experiment involves adding [(DMSC)Ti{1,2,4-$(Me_3Si)_3C_6H_3$}] (**1**) into a hydrocarbon solution of alkyne (≥2 equiv) and ketone (2 equiv). When the reaction was monitored in C_6D_6 by ^{1}H NMR, near quantitative formation of **20**−**25** was observed, along with small amounts of alkyne cyclotrimerization products. The conversion of **1** to **22**−**25** is near completion in 5−10 min, whereas the complete conversion of **1** into **20** or **21** requires several hours. This trend is similar to the relative rates observed for the formation of complexes **5**−**16**. An excess of alkyne was employed in the reactions to ensure the complete conversion of **1** to **20**−**25**. This is because the product distribution obtained in the reactions depends on the rates of two competing reactions since **1** is capable of reacting with alkynes and ketones (Scheme 4). If **1** reacts with the alkyne at a much faster rate than it does with the ketone ($k_1 \gg k_2$), then the reaction leads to predominant formation of **20**−**25**. If $k_2 \gg k_1$, then the reaction proceeds to give the corresponding products of the reactions of ketones with **1** and the alkyne does not participate.[33] If $k_1 \approx k_2$, then products of both reaction pathways are formed.

Compounds **20**, **22**, and **24** were isolated and characterized, and the other compounds were characterized

Scheme 4



R = $SiMe_3$

[Ti] = (DMSC)Ti

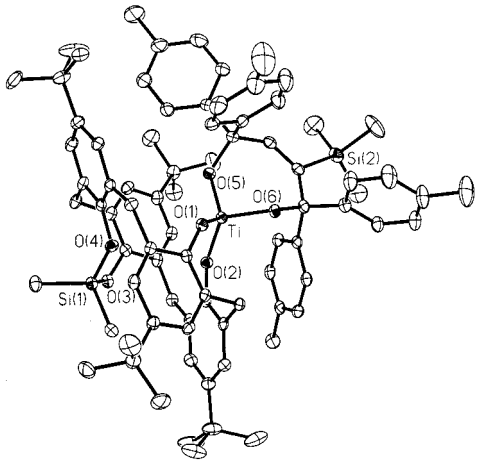


Figure 2. Molecular structure of **20** (30% probability ellipsoids).

Table 2. Selected Bond Distances and Angles for 20

Bond Distances, Å	
Ti−O(1)	1.8192(19)
Ti−O(2)	1.8056(19)
Ti−O(5)	1.800(2)
Ti−O(6)	1.7941(19)
Bond Angles, deg	
O(1)−Ti−O(2)	105.94(9)
O(1)−Ti−O(5)	115.84(9)
O(1)−Ti−O(6)	107.99(9)
O(2)−Ti−O(5)	114.98(9)
O(2)−Ti−O(6)	114.71(9)
O(5)−Ti−O(6)	97.35(9)

in-situ. The solution NMR studies are consistent with existence of **20**−**25** in 1,2-alternate conformation and with their C_s symmetry at 22 °C on the NMR time scale. However, **23**−**25** display broadened resonances at 22 °C. Variable-temperature ^{1}H NMR study of **24** showed that the peaks become sharp below 0 °C, but increasingly broaden as the temperature is increased up to 100 °C. Presumably, motion of the flexible substituent on the double bond (CH_2OMe, CH_2NMe_2, or CH_2OSiMe_3) accounts for this broadening of the NMR signals. The spectral characteristics of the DMSC ligands of complexes with similar metallacycle endo-fragments (**20** and **21**, Ar_2CO; **22**−**25**, $C_6H_{10}O$) are nearly identical. The metallacycle CH proton resonates at δ 5.83−6.05 ppm in **22**−**25**; the corresponding resonance in **20** and **21** is obstructed by aromatic resonances. The solid-state structure of **20** was determined by X-ray crystallography (Figure 2). It confirmed 1,2-alternate conformation of the DMSC ligand, albeit heavily distorted by the need to accommodate the *endo*-Tol_2C group (Tol = 4-Me-C_6H_4). That the Me_3Si group is on the exo-end of the double bond of the dioxatitanacycloheptene is also confirmed. The crystallographic data and selected bond distances and angles for **20** are listed in Tables 1 and 2, respectively. All the Ti−O distances fall within 1.794−1.819 Å, the expected range for Ti−O distance in a four-coordinate Ti(IV) complex. The geometrical parameters of the dioxatitanacycloheptene ring are consistent with its formulation. The titanacycle is distorted (Figure 2) due to unfavorable steric interaction of the *p*-tolyl substituents with the DMSC ligand, and the structure is C_1-symmetric. The C_s symmetry observed in solution may be explained by a rapid equilibration between two C_1-symmetric forms.

Mechanistic Considerations. Compounds **20**−**25** are products of two ketone insertions into two Ti−C bonds. These insertions are undoubtedly sequential, and given that the two acetylenic carbons are different and that there are two possible alkyne orientations with respect to the DMSC ligand, four insertion sequences are possible. On the basis of exclusive exo-orientation of the alkyne non-H substituent in titanium η^2-alkyne complexes **5**−**16** and exo-orientation of the Me_3Si group of **20** in the solid state (vide supra), it is reasonable to suggest that insertion sequences involving (DMSC)Ti(η^2-alkyne) species in which the alkyne non-H substituent is endo-oriented are highly unlikely. Therefore, using the formation of **20** as an example, only the two remaining insertion sequences will be considered (Scheme 4). Tol_2CO can insert either into the *exo*- or the *endo*-Ti−C bond of the η^2-alkyne species (DMSC)Ti($Me_3SiC\equiv$CH) (**I**). Insertion into the *endo*-Ti−C bond would produce 2-oxatitanacyclopent-4-ene derivative **II**, which has the $SiMe_3$ group bonded at the 5-position. In contrast, insertion into the *exo*-Ti−C bond would produce the regioisomer **III**, which has the $SiMe_3$ group bonded at the 4-position. We have synthesized compound **II** by an independent route and established that it does not react with Tol_2CO.[45] In fact, it appears that the insertion of a ketone into the Ti−C bond of a 2-oxatitanacyclopentene species observed here is unusual. The reported 2-oxatitanacyclopentene compounds supported by bis(alkoxy)-,[1k] bis(aryloxy)-,[25] and bis(cyclopentadienyl)[46] ligand systems do not react with ketones. However, in all of these cases the 5-position (α-carbon) of the 2-oxatitanacyclopentene bears a substituent. We can only conclude that the insertion of a ketone into the Ti−C bond of a 2-oxatitanacyclopentene can occur if the α-carbon does not bear a substituent. Effectively, this means that a dioxatitanacycloheptene will form only if the first insertion occurs at the substituted end of the terminal alkyne. That the DMSC ligand exerts a directing influence over the approach of a reactant toward DMSC-based Ti species has been established.[30−33] Thus, preferentially approach of the ketone via the more open exo-face of the titanacyclopropene species **I** promotes initial exo-insertion. However, the DMSC ligand does not prevent a subsequent endo-insertion.[47] The formation of **20** and **21** can be conveniently monitored by ^{1}H NMR spectroscopy. In both cases, the only species observed in solution during the course of the reaction are the reactants, 1,2,4-($Me_3Si)_3C_6H_3$, along with **20** and **21**, respectively. This implies that $k_3 \gg k_1$ and $k_4 \gg k_3$ (Scheme 4), and hence, the rate-limiting step of the formation of **20** and **21** is the displacement of the coordinated arene by $Me_3SiC\equiv$CH.

(45) Ozerov, O. V.; Parkin, S.; Brock, C. P.; Ladipo, F. T. *J. Chem. Soc., Chem. Commun.*, submitted. This result also rules out possible isomerization of **II** to **III** under our reaction conditions.

(46) Shur, V. B.; Burlakov, V. V.; Yanovsky, A. I.; Petrovsky, P. V.; Struchkov, Yu. T.; Vol'pin, M. E. *J. Organomet. Chem.* **1985**, *297*, 51.

(47) We have characterized a compound formed by insertion of a cyclohexanone molecule into the endo Ti−C bond of [(DMSC)Ti(1,2,4-($Me_3Si)_3C_6H_3$)] (**1**) by X-ray crystallography.[33]

Conclusion

The directing influence of the DMSC ligand is strongly manifested in the reactions of [(DMSC)Ti{1,2,4-$(Me_3Si)_3C_6H_3$}] (**1**). Thus, "(DMSC)Ti" mediates coupling of terminal alkynes with ketones to produce 2,7-dioxa-1-titana-4-cycloheptenes. The regioselectivity of the reaction is controlled by the steric environment of the DMSC ligand that enforces exo-orientation of the alkyne non-H substituent in the putative intermediate (DMSC)Ti(η^2-alkyne) species. The chemoselectivity of the reaction can be tailored on the basis of knowledge of the rates of reaction of alkynes and ketones with **1**. Studies of related complexes and reactions are in progress in our laboratory.

Experimental Section

General Details. All experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. glovebox. Tetrahydrofuran, ether, and toluene were distilled twice from sodium benzophenone ketyl. Pentane was distilled twice from sodium benzophenone ketyl with addition of 1 mL/L of tetraethylene glycol dimethyl ether as a solubilizing agent. Benzene-d_6 was distilled from sodium benzophenone ketyl. All solvents were stored in the glovebox over 4 Å molecular sieves that were dried in a vacuum oven at 150 °C for at least 48 h prior to use. Alkynes, bipyridines, ketones, and aldehydes were purchased from Aldrich or Farchan and were distilled from CaH_2 prior to use. ^{1}H (200 MHz) and ^{13}C (50.3 MHz) NMR spectra were recorded on a Varian Gemini-200 spectrometer at ca. 22 °C. ^{1}H and ^{13}C chemical shifts were referenced to residual solvent peaks. GC−MS analyses were performed on a Hewlett-Packard 5890 series II gas chromatograph with a Hewlett-Packard 5972 series mass selective detector at an ionizing potential of 70 eV.

General Procedure for in-Situ Synthesis of [(DMSC)Ti(alkyne)(L_2)] (L_2 = bpy or dmbpy). [(DMSC)Ti{$C_6H_3(SiMe_3)_3$}] (**1**) in C_6D_6 (0.500 mL of 0.04 M stock solution, 0.020 mmol) was introduced into an NMR tube. Next, 0.120 mL of a 0.20 M (0.024 mmol) stock solution of either bpy or dmbpy in C_6D_6 was added. A 0.060 mmol sample of alkyne was introduced into the resulting solution by means of a microsyringe, and the NMR tube was capped and vigorously shaken for 30 s. Under these conditions the transformation is complete in under 15 min, except in the case of $Me_3SiC{\equiv}CH$ and $Bu^tC{\equiv}CH$, which require longer reaction times. After completion, reaction mixtures typically contained only the following: the Ti product, 1,2,4-tris(trimethylsilyl)benzene, excess alkyne and bpy (or dmbpy), and traces of alkyne cyclotrimerization products. The products were identified by ^{1}H NMR. This procedure is applicable to all of the alkyne complexes listed below. In those cases when the isolation and purification of the product were performed, appropriate procedures are described and additional spectral and analytical data are provided.

[(DMSC)Ti(HC≡CSiMe$_3$)(bpy)] (5). [(DMSC)Ti{$C_6H_3(SiMe_3)_3$}] (**1**) (0.418 g, 0.400 mmol) and bpy (0.062 g, 0.400 mmol) were dissolved in 15 mL of pentane, and $Me_3SiC{\equiv}CH$ (0.227 mL, 1.60 mmol) was added to this solution. It was stirred for 24 h, during which time blue precipitate separated. It was filtered off, washed with an additional 5 mL of pentane, and dried in vacuo to give 0.39 g (97%) of the product as a blue solid. ^{1}H NMR (C_6D_6) δ: bpy, 9.60(d, 2H), 7.14(d, 2H), 6.79(t, 2H), 6.37(t, 2H); HC≡CSiMe$_3$, 8.08(s, 1H, HC≡CSiMe$_3$), −0.59(s, 9H, SiMe$_3$); DMSC, 7.39 (d, 2H, arom CH), 7.29(d, 2H, arom CH), 7.22(d, 2H, arom CH), 7.10(d, 2H, arom CH), 4.78(d, J = 14 Hz, 1H, calix-CH_2), 4.56(d, J = 17 Hz, 2H, calix-CH_2), 4.43(d, J = 17 Hz, 2H, calix-CH_2), 3.58(d, J = 14 Hz, 1H, calix-CH_2), 2.96(d, J = 13 Hz, 1H, calix-CH_2), 2.31(d, J = 13 Hz, 1H, calix-CH_2), 1.40(s, 18H, t-Bu), 1.33(s, 18H, t-Bu), 0.52(s, 3H, exo-SiMe), −1.06(endo-SiMe).

[(DMSC)Ti(*p*-TolC≡CH)(bpy)] (6) (dark green-blue solution in C_6D_6). ^{1}H NMR (C_6D_6) δ: bpy, 9.52(d, 2H), 6.88(d, 2H), 6.71(t, 2H), 6.40(t, 2H); HC≡CTol, 7.38(s, 1H, HC≡CTol), 6.45(d, J = 8 Hz, 2H, arom), 5.54(d, J = 8 Hz, 2H, arom), 1.91(s, 3H, CH_3); DMSC, 7.40 (d, 2H, arom CH), 7.26−7.30(2 doublets, 4H, arom CH), 7.18(d, 2H, arom CH), 4.78(d, J = 14 Hz, 1H, calix-CH_2), 4.57(d, J = 17 Hz, 2H, calix-CH_2), 4.46(d, J = 17 Hz, 2H, calix-CH_2), 3.55(d, J = 14 Hz, 1H, calix-CH_2), 3.11(d, J = 13 Hz, 1H, calix-CH_2), 2.80(d, J = 13 Hz, 1H, calix-CH_2), 1.38(s, 18H, t-Bu), 1.33(s, 18H, t-Bu), 0.56(s, 3H, exo-SiMe), −1.00(endo-SiMe).

[(DMSC)Ti(HC≡CBu^t)(bpy)] (7). [(DMSC)Ti{$C_6H_3(SiMe_3)_3$}] (**1**) (0.314 g, 0.300 mmol) and bpy (0.047 g, 0.300 mmol) were dissolved in 10 mL of pentane/toluene (10:1), and t-BuC≡CH (0.110 mL, 0.90 mmol) was added to this solution. It was allowed to stand for 24 h at ambient temperature, during which time purplish-brown precipitate separated. It was filtered off, washed with pentane until washings were colorless, and dried in vacuo to give 0.295 g (93%) of the product. One equivalent of pentane per Ti was retained by the product after prolonged drying in vacuo. Anal. Calcd for $C_{62}H_{76}N_2O_4SiTi$: C, 75.28; H, 7.74; N, 2.83. Found: C, 75.72; H, 7.46; N, 2.63. ^{1}H NMR (C_6D_6) δ: bpy, 9.54(d, 2H), 7.06(d, 2H), 6.78(t, 2H), 6.35(t, 2H); HC≡CCMe$_3$, 7.45(s, 1H, HC≡CCMe$_3$), 0.45(s, 9H, CMe$_3$); DMSC, 7.41 (d, 2H, arom CH), 7.31(d, 2H, arom CH), 7.23(d, 2H, arom CH), 7.12(d, 2H, arom CH), 4.81(d, J = 14 Hz, 1H, calix-CH_2), 4.58(d, J = 17 Hz, 2H, calix-CH_2), 4.44(d, J = 17 Hz, 2H, calix-CH_2), 3.60(d, J = 14 Hz, 1H, calix-CH_2), 2.93(d, J = 13 Hz, 1H, calix-CH_2), 2.34(d, J = 13 Hz, 1H, calix-CH_2), 1.44(s, 18H, t-Bu), 1.34(s, 18H, t-Bu), 0.52(s, 3H, exo-SiMe), −1.05(endo-SiMe). ^{13}C NMR (CD_2Cl_2) δ: 200.5(HC≡CBu^t), 190.2(HC≡CBu^t), 160.2(TiOC), 151.1(br, 2C), 150.2, 143.1, 139.0, 137.4, 131.5, 131.0, 129.2, 127.8, 126.5, 125.5, 124.5, 124.4, 123.4, 121.4, 41.5(2C, calix-CH_2), 37.3(calix-CH_2), 36.5(calix-CH_2), 34.5(HC≡CC$(CH_3)_3$), 34.0(calix-C$(CH_3)_3$), 33.9(calix-C$(CH_3)_3$), 31.9(calix-C$(CH_3)_3$), 31.8(calix-C$(CH_3)_3$), 30.5(HC≡CC$(CH_3)_3$), 4.3(exo-SiCH_3), −2.7(endo-SiCH_3).

[(DMSC)Ti(HC≡CCH$_2$OSiMe$_3$)(bpy)] (8) (dark-purple solution in C_6D_6). ^{1}H NMR (C_6D_6) δ: bpy, 9.47(d, 2H), 7.08(d, 2H), 6.81(t, 2H), 6.39(t, 2H); HC≡CCH$_2$OSiMe$_3$, 7.34(br s, 1H, HC≡C), 3.94(d, J = 1 Hz, 2H, CH_2), −0.31(s, 9H, SiMe$_3$); DMSC, 7.35 (d, 2H, arom CH), 7.28(d, 2H, arom CH), 7.24(d, 2H, arom CH), 7.14(d, 2H, arom CH), 4.77(d, J = 14 Hz, 1H, calix-CH_2), 4.54(d, J = 17 Hz, 2H, calix-CH_2), 4.43(d, J = 17 Hz, 2H, calix-CH_2), 3.56(d, J = 14 Hz, 1H, calix-CH_2), 3.03(d, J = 13 Hz, 1H, calix-CH_2), 2.54(d, J = 13 Hz, 1H, calix-CH_2), 1.35(br s, 36H, t-Bu), 0.53(s, 3H, exo-SiMe), −1.04(endo-SiMe).

[(DMSC)Ti(HC≡CCH$_2$NMe$_2$)(bpy)] (9) (dark-blue solution in C_6D_6). ^{1}H NMR (C_6D_6) δ: bpy, 9.51(d, 2H), 7.08(d, 2H), 6.82(t, 2H), 6.40(t, 2H); HC≡CCH$_2$NMe$_2$, 7.35(br s, 1H, HC≡C), 2.38(d, J = 1 Hz, 2H, CH_2), 1.42(s, 9H, NMe$_2$); DMSC, 7.34 (d, 2H, arom CH), 7.28(d, 2H, arom CH), 7.25(d, 2H, arom CH), 7.17(d, 2H, arom CH), 4.77(d, J = 14 Hz, 1H, calix-CH_2), 4.56(d, J = 17 Hz, 2H, calix-CH_2), 4.44(d, J = 17 Hz, 2H, calix-CH_2), 3.56(d, J = 14 Hz, 1H, calix-CH_2), 3.09(d, J = 13 Hz, 1H, calix-CH_2), 2.65(d, J = 13 Hz, 1H, calix-CH_2), 1.37(s, 18H, t-Bu), 1.35(s, 18H, t-Bu), 0.53(s, 3H, exo-SiMe), −1.03(endo-SiMe).

[(DMSC)Ti(HC≡CCH$_2$CH$_2$CH$_3$)(bpy)] (10) (dark-blue solution in C_6D_6). ^{1}H NMR (C_6D_6) δ: bpy, 9.52(d, 2H), 7.14(d, 2H), 6.76(t, 2H), 6.35(t, 2H); HC≡CCH$_2$CH$_2$CH$_3$, 7.23(br s, 1H, HC≡C), 2.38(d, J = 1 Hz, 2H, CH_2), 1.42(s, 9H, NMe$_2$); DMSC, 7.35 (d, 2H, arom CH), 7.27(d, 2H, arom CH), 7.25(d, 2H, arom CH), 7.16(d, 2H, arom CH), 4.78(d, J = 14 Hz, 1H, calix-CH_2), 4.56(d, J = 17 Hz, 2H, calix-CH_2), 4.44(d, J = 17 Hz, 2H, calix-CH_2), 3.56(d, J = 14 Hz, 1H, calix-CH_2), 3.07(d, J = 13 Hz, 1H, calix-CH_2), 2.60(d, J = 13 Hz, 1H, calix-CH_2), 1.37(s, 18H, t-Bu), 1.35(s, 18H, t-Bu), 0.53(s, 3H, exo-SiMe), −1.02(endo-SiMe).

[(DMSC)Ti(HC≡CSiMe$_3$)(dmbpy)] (11). Method 1. A 25 mL reaction vessel equipped with a Teflon stopcock was charged with [(DMSC)Ti(C≡CSiMe$_3$)$_2$(dmbpy)] (**3**) (0.480 g, 0.40 mmol), Me$_3$SiC≡CH (0.112 mL, 0.70 mmol), and 15 mL of toluene. The vessel was heated at 80 °C for 1.5 h. After that the volatiles were removed, and solids were triturated with heptane and washed with 10 mL of pentane. After drying in vacuo, 0.256 g (64%) of product was obtained. **Method 2**. A 25 mL Schlenk flask was charged with (DMSC)TiCl$_2$ (**4**) (0.493 g, 0.60 mmol), 4,4′-dimethyldipyridyl (0.110 g, 0.60 mmol), and 15 mL of THF. This mixture was stirred until all of the contents dissolved. Then 0.018 g (0.75 mmol) of Mg powder and 0.340 mL (2.4 mmol) of Me$_3$SiC≡CH were added to the solution, and it was stirred for 18 h. After that the volatiles were removed from the deep-blue solution in vacuo, and solids were triturated with heptane, extracted with toluene, and filtered. The volatiles were removed from the filtrate in vacuo, then it was triturated with heptane, washed with pentane, and dried in vacuo to give blue solid. Yield: 0.417 g (69%). Anal. Calcd for $C_{63}H_{80}N_2O_4Si_2Ti$: C, 73.22; H, 7.80; N, 2.71. Found: C, 73.28; H, 7.88; N, 2.72. ^{1}H NMR (C_6D_6) δ: dmbpy, 9.42(d, 2H, arom), 7.12−7.15(br, dmbpy(2H), calix arom CH(2H) and C_6D_5H), 6.22(d, 2H, dmbpy), 1.71(s, 6H, CH$_3$); HC≡CSiMe$_3$, 8.18(s, 1H, HC≡CSiMe$_3$), −0.51(s, 9H, SiMe$_3$); DMSC, 7.40 (d, 2H, arom CH), 7.33(d, 2H, arom CH), 7.23(d, 2H, arom CH), 7.12−7.15(br, dmbpy(2H), calix arom CH(2H) and C_6D_5H), 4.78(d, J = 14 Hz, 1H, calix-CH$_2$), 4.56(d, J = 17 Hz, 2H, calix-CH$_2$), 4.43(d, J = 17 Hz, 2H, calix-CH$_2$), 3.59(d, J = 14 Hz, 1H, calix-CH$_2$), 3.02(d, J = 13 Hz, 1H, calix-CH$_2$), 2.38(d, J = 13 Hz, 1H, calix-CH$_2$), 1.43(s, 18H, t-Bu), 1.34(s, 18H, t-Bu), 0.54(s, 3H, exo-SiMe), −1.04(endo-SiMe). ^{13}C NMR (C_6D_6) δ: 208.4(HC≡CSiMe$_3$), 190.8(HC≡CSiMe$_3$), 160.5(TiOC), 150.5, 150.1, 149.9, 147.7, 142.8, 139.4, 131.6, 131.3, 129.5, 128.3, 127.8, 126.4, 125.8, 124.7, 124.6, 124.1, 42.1(calix-CH$_2$), 38.3-(calix-CH$_2$), 36.3(calix-CH$_2$), 34.0(C(CH$_3$)$_3$), 33.9(C(CH$_3$)$_3$), 32.0-(br, C(CH$_3$)$_3$), 20.8(dmbpy), 4.6(exo-SiMe), 0.2(HC≡CSiMe$_3$), −2.4(endo-SiMe).

[(DMSC)Ti(*p*-TolC≡CH)(dmbpy)] (12). A 25 mL Schlenk flask was charged with [(DMSC)Ti(C≡CSiMe$_3$)$_2$(dmbpy)] (**3**) (0.72 g, 0.60 mmol), 4-ethynyltoluene (0.15 mL, 1.2 mmol), and 15 mL of toluene. The vessel was heated at 80 °C for 1.5 h, during which the solution turned deep-blue. After that the volatiles were removed and solids were triturated with heptane and washed with 10 mL of pentane. The product was then dried in vacuo to give 0.309 g (49%) as a dark greenish-blue solid. Anal. Calcd for $C_{57}H_{78}N_2O_4SiTi$: C, 76.54; H, 7.48; N, 2.66. Found: C, 76.34; H, 7.57; N, 2.62. ^{1}H NMR (C_6D_6) δ: dmbpy, 9.38(d, J = 6 Hz, 2H, arom), 6.91(s, 2H, arom), 6.27-(d, J = 6 Hz, 2H, arom), 1.66(s, 6H, CH$_3$); HC≡CTol, 7.47(s, 1H, HC≡CTol), 6.46(d, J = 8 Hz, 2H, arom), 5.76(d, J = 8 Hz, 2H, arom), 1.88(s, 3H, CH$_3$); DMSC, 7.43 (d, 2H, arom CH), 7.32(d, 2H, arom CH), 7.29(d, 2H, arom CH), 7.21(d, 2H, arom, CH), 4.81(d, J = 14 Hz, 1H, calix-CH$_2$), 4.53(d, J = 17 Hz, 2H, calix-CH$_2$), 4.49(d, J = 17 Hz, 2H, calix-CH$_2$), 3.58(d, J = 14 Hz, 1H, calix-CH$_2$), 3.15(d, J = 13 Hz, 1H, calix-CH$_2$), 2.80(d, J = 13 Hz, 1H, calix-CH$_2$), 1.39(s, 18H, t-Bu), 1.36(s, 18H, t-Bu), 0.58(s, 3H, exo-SiMe), −0.98(endo-SiMe); ^{13}C NMR (C_6D_6) δ: 189.5(HC≡CTol), 186.3(HC≡CTol), 160.4(TiOC), 150.6, 149.4, 149.3, 147.1, 143.1, 140.7, 139.7, 132.0, 131.7, 131.2, 130.0, 128.4, 127.7, 125.2, 124.7, 124.3, 122.2, 121.2, 42.2(calix-CH$_2$), 38.1(calix-CH$_2$), 36.3(calix-CH$_2$), 34.0(br, C(CH$_3$)$_3$), 32.0(C(CH$_3$)$_3$), 31.9(C(CH$_3$)$_3$), 20.8(tolyl), 20.5(dmbpy), 4.7(exo-SiMe), −2.3(endo-SiMe).

[(DMSC)Ti(HC≡CBu^t)(dmbpy)] (13) (dark-blue solution in C_6D_6). ^{1}H NMR (C_6D_6) δ: dmbpy, 9.38(d, 2H, arom), 7.13-(br, 2H), 6.23(d, 2H, dmbpy), 1.70(s, 6H, CH$_3$); HC≡CCMe$_3$, 7.49(s, 1H, HC≡CCMe$_3$), 0.53(s, 9H, CMe$_3$); DMSC, 7.41 (d, 2H, arom CH), 7.32(d, 2H, arom CH), 7.23(d, 2H, arom CH), 7.13(d, 2H, arom CH), 4.81(d, J = 14 Hz, 1H, calix-CH$_2$), 4.58-(d, J = 17 Hz, 2H, calix-CH$_2$), 4.45(d, J = 17 Hz, 2H, calix-CH$_2$), 3.61(d, J = 14 Hz, 1H, calix-CH$_2$), 2.98(d, J = 13 Hz, 1H, calix-CH$_2$), 2.39(d, J = 13 Hz, 1H, calix-CH$_2$), 1.45(s, 18H, t-Bu), 1.34(s, 18H, t-Bu), 0.52(s, 3H, exo-SiMe), −1.04(endo-SiMe).

[(DMSC)Ti(HC≡CCH$_2$OSiMe$_3$)(dmbpy)] (14) (dark-purple solution in C_6D_6). ^{1}H NMR (C_6D_6) δ: dmbpy, 9.30(d, 2H, arom), 7.13(s, 2H, arom), 6.24(d, 2H, arom), 1.73(s, 6H, CH$_3$); HC≡CCH$_2$OSiMe$_3$, 7.41(br s, 1H, HC≡C), 4.06(br s, 2H, CH$_2$), −0.28(s, 9H, SiMe$_3$); DMSC, 7.38 (d, 2H, arom CH), 7.30(d, 2H, arom CH), 7.25(d, 2H, arom CH), 7.17(d, 2H, arom CH), 4.79(d, J = 14 Hz, 1H, calix-CH$_2$), 4.56(d, J = 17 Hz, 2H, calix-CH$_2$), 4.45(d, J = 17 Hz, 2H, calix-CH$_2$), 3.58(d, J = 14 Hz, 1H, calix-CH$_2$), 3.10(d, J = 13 Hz, 1H, calix-CH$_2$), 2.60(d, J = 13 Hz, 1H, calix-CH$_2$), 1.38(s, 18H, t-Bu), 1.36(s, 18H, t-Bu), 0.54(s, 3H, exo-SiMe), −1.02(endo-SiMe).

[(DMSC)Ti(HC≡CCH$_2$NMe$_2$)(dmbpy)] (15) (dark purplish-blue solution in C_6D_6). ^{1}H NMR (C_6D_6) δ: dmbpy, 9.36(d, 2H, arom), 7.14(s, 2H, arom), 6.24(d, 2H, arom), 1.73(s, 6H, CH$_3$); HC≡CCH$_2$NMe$_2$, 7.45(br s, 1H, HC≡C), 2.48(d, J = 1 Hz, 2H, CH$_2$), 1.56(s, 9H, NMe$_2$); DMSC, 7.45 (d, 2H, arom CH), 7.31-(d, 2H, arom CH), 7.27(d, 2H, arom CH), 7.19(d, 2H, arom CH), 4.79(d, J = 14 Hz, 1H, calix-CH$_2$), 4.59(d, J = 17 Hz, 2H, calix-CH$_2$), 4.46(d, J = 17 Hz, 2H, calix-CH$_2$), 3.59(d, J = 14 Hz, 1H, calix-CH$_2$), 3.13(d, J = 13 Hz, 1H, calix-CH$_2$), 2.67(d, J = 13 Hz, 1H, calix-CH$_2$), 1.39(s, 18H, t-Bu), 1.38(s, 18H, t-Bu), 0.54(s, 3H, exo-SiMe), −1.01(endo-SiMe).

[(DMSC)Ti(HC≡CCH$_2$CH$_2$CH$_3$)(dmbpy)] (16) (dark-blue solution in C_6D_6). ^{1}H NMR (C_6D_6) δ: dmbpy, 9.39(d, 2H, arom), 7.16(s, 2H, arom), 6.22(d, 2H, arom), 1.71(s, 6H, CH$_3$); HC≡CCH$_2$CH$_2$CH$_3$, 7.34(br s, 1H, HC≡C), 1.28(br t, 2H, α-CH$_2$), 0.85−1.0(m, 2H, β-CH$_2$), 0.49(t, J = 7 Hz, 3H, CH$_3$); DMSC: 7.38 (d, 2H, arom CH), 7.30(d, 2H, arom CH), 7.26(d, 2H, arom CH), 7.18(d, 2H, arom CH), 4.79(d, J = 14 Hz, 1H, calix-CH$_2$), 4.59(d, J = 17 Hz, 2H, calix-CH$_2$), 4.47(d, J = 17 Hz, 2H, calix-CH$_2$), 3.59(d, J = 14 Hz, 1H, calix-CH$_2$), 3.11(d, J = 13 Hz, 1H, calix-CH$_2$), 2.61(d, J = 13 Hz, 1H, calix-CH$_2$), 1.38(s, 18H, t-Bu), 1.37(s, 18H, t-Bu), 0.54(s, 3H, exo-SiMe), −1.01(endo-SiMe).

[(DMSC)TiPh$_2$] (17). A suspension of (DMSC)TiCl$_2$ (**4**) (0.822 g, 1.00 mmol) in 10 mL of toluene was treated with solid Ph$_2$Mg·2THF (0.322 g, 1.00 mmol) at ambient temperature. The resulting mixture was stirred for 30 min and then filtered. The volatiles were removed from the filtrate in vacuo, and the residue was washed with a small amount of pentane and dried in vacuo to give 0.75 g (83%) of the product as yellow powder. Anal. Calcd for $C_{58}H_{68}O_4SiTi$: C, 76.96; H, 7.57; Cl, 0.00. Found: C, 76.79; H, 7.31; Cl, <0.03. ^{1}H NMR (C_6D_6) δ: 7.87−7.92(m, 2H, Ph), 7.28(d, J = 2 Hz, 2H, calix arom), 7.19(d, J = 2 Hz, 2H, calix arom), 7.12(d, J = 2 Hz, 2H, calix arom), 6.9−7.0(m, 6H), 6.77(t, 2H, J = 7.5 Hz, Ph), 6.54(d, 2H, J = 7.5 Hz, Ph), 4.48(d, 2H, J = 17 Hz, calix-CH$_2$), 4.44(d, 1 H, J = 15 Hz, calix-CH$_2$), 4.29(d, 1 H, J = 14 Hz, calix-CH$_2$), 4.03-(d, 2H, J = 17 Hz, calix-CH$_2$), 3.40(d, 1 H, J = 15 Hz, calix-CH$_2$), 3.18(d, 1 H, J = 14 Hz, calix-CH$_2$), 1.31(s, 18 H, t-Bu), 1.22(s, 18 H, t-Bu), 0.18(s, 3 H, exo-SiMe), −1.40(s, 3 H, endo-SiMe). ^{13}C NMR ($CDCl_3$) δ: 196.7(TiC), 195.9(TiC), 159.2-(TiOC), 149.3(SiOC), 144.7, 143.7, 134.9, 131.6, 131.4, 129.7, 129.6, 129.2, 128.3, 127.5, 126.9, 126.8, 126.5, 126.2, 126.1, 125.5, 39.1(calix-CH$_2$), 37.3(calix-CH$_2$), 37.0(calix-CH$_2$), 34.1-(C(CH$_3$)$_3$), 33.7(C(CH$_3$)$_3$), 31.5(C(CH$_3$)$_3$), 31.4(C(CH$_3$)$_3$), 2.9(exo-SiMe), −3.0(endo-SiMe).

[(DMSC)Ti(bpy)$_2$] (18). To a solution of (DMSC)TiPh$_2$ (**17**) (0.655 g, 0.724 mmol) in 15 mL of pentane/1 mL THF was added bipyridine (0.237 g, 1.52 mmol). The reaction mixture immediately turned dark blue, and it was stirred for 1 h. The resulting solution was filtered, and the blue precipitate was washed with 5 mL of pentane and dried in vacuo to give 0.74 g (96%) of the crude material, containing minor amounts of C_6H_5−C_6H_5 and bipyridine. Recrystallization from THF/pentane afforded 0.57 g (74%) of analytically pure product. Anal. Calcd for $C_{66}H_{74}N_4O_4SiTi$: C, 74.55; H, 7.01; N, 5.27. Found: C, 74.24; H, 6.86; N, 4.98. ^{1}H NMR (C_6D_6) δ: 9.72(d, 2H, J =

6 Hz, bpy), 9.34(d, 2H, J = 6 Hz, bpy), 7.42 (d, 2H, arom CH), 7.39(d, 2H, arom CH), 7.04(d, 2H, J = 8 Hz, bpy), 6.99(d, 2H, arom CH), 6.79(d, 2H, J = 8 Hz, bpy), 6.76(d, 2H, arom CH), 6.51(t, 2H, bpy), 6.07(t, 2H, bpy), 5.81(t, 2H, bpy), 5.66(t, 2H, bpy), 4.77(d, 2H, J = 17 Hz, calix-CH_2), 4.51(d, 1H, J = 14 Hz, calix-CH_2), 4.33(d, 2H, J = 17 Hz, calix-CH_2), 3.70(d, 1H, J = 14 Hz, calix-CH_2), 3.31(d, 1H, J = 14 Hz, calix-CH_2), 3.17-(d, 1H, J = 14 Hz, calix-CH_2), 1.47(s, 18H, t-Bu), 0.99(s, 18H, t-Bu), 0.26(s, 3H, exo-SiMe), −0.87(endo-SiMe). ^{13}C NMR (C_6D_6) δ: 162.6(TiOC), 151.6(SiOC), 147.0, 146.5, 142.4, 139.8, 138.0, 137.4, 131.7, 131.3, 129.8, 129.6, 128.3, 127.9, 127.2, 127.0, 126.4, 125.7, 121.6, 121.5, 114.1, 113.7, 40.8(calix-CH_2), 38.0(br s, calix-CH_2), 34.0($C(CH_3)_3$), 33.6($C(CH_3)_3$), 32.0-($C(CH_3)_3$), 31.5($C(CH_3)_3$), 2.4(exo-SiMe), −1.8(endo-SiMe).

[(DMSC)Ti(dmbpy)$_2$] (19). 4,4′-Dimethyldipyridyl (0.046 g, 0.250 mmol) was dissolved in 10 mL of THF, and Na metal (0.023 g, 1.00 mmol) was added to this solution. It was stirred for 2 h, becoming purple and then brown. This brown solution was filtered into a solution of (DMSC)$TiCl_2$(dmbpy) (0.252 g, 0.250 mmol) (see below) in 20 mL of THF. The mixture turned dark-blue instantly. It was stirred for 45 min, then the amount of THF was reduced to ca. 20 mL and it was filtered. The filtrate was concentrated to ca. 8 mL, layered with 15 mL of pentane, and then cooled to −20 °C. After standing overnight, a dark-blue precipitate was separated, washed with pentane until the washings were almost colorless, and dried in vacuo. Yield: 0.160 g (54%). ^{1}H NMR (C_6D_6) δ: 9.67 (d, 2H, J = 6 Hz, dmbpy), 9.23(d, 2H, J = 6 Hz, bpy), 7.48(br s, 4H, dmbpy), 7.07(d, 2H, arom CH), 6.99(d, 2H, arom CH), 6.77(d, 2H, arom CH), 6.71(d, 2H, arom CH), 5.56(d, 2H, J = 6 Hz, dmbpy), 5.45-(d, 2H, J = 6 Hz, dmbpy), 4.79(d, 2H, J = 17 Hz, calix-CH_2), 4.57(d, 1H, J = 14 Hz, calix-CH_2), 4.33(d, 2H, J = 17 Hz, calix-CH_2), 3.92(d, 1H, J = 14 Hz, calix-CH_2), 3.35(d, 1H, J = 14 Hz, calix-CH_2), 3.28(d, 1H, J = 14 Hz, calix-CH_2), 1.95(s, 3H, dmbpy), 1.69(s, 3H, dmbpy), 1.50(s, 18H, t-Bu), 1.01(s, 18H, t-Bu), 0.29(s, 3H, exo-SiMe), −0.78(s, 3H, endo-SiMe). ^{13}C NMR (C_6D_6) δ: 162.9(TiOC), 151.7(SiOC), 146.7, 146.2, 142.2, 140.7, 139.2, 137.8, 137.5, 137.2, 131.7, 131.1, 129.5, 127.9, 127.2, 126.8, 126.4, 125.6, 121.9, 121.4, 116.0, 115.3, 40.7(calix-CH_2), 38.2(calix-CH_2), 38.0(calix-CH_2), 34.0($C(CH_3)_3$), 33.5-($C(CH_3)_3$), 32.1($C(CH_3)_3$), 31.4($C(CH_3)_3$), 20.3(CH_3, dmbpy), 19.9(CH_3, dmbpy), 2.2(exo-SiMe), −1.8(endo-SiMe).

[(DMSC)$TiCl_2$(dmbpy)]. To 1.97 g (2.40 mmol) of (DMSC)-$TiCl_2$ (**4**) was added 50 mL of a 1:1 mixture of Et_2O and THF and then a solution of 0.420 g (2.28 mmol) of 4,4′-dimethyldipyridyl in 25 mL of THF. The resulting suspension was stirred for 2 h, then the volatiles were removed in vacuo. The residue was washed on the fritted funnel with 30 mL of a 5:1 Et_2O/THF mixture, then with 10 mL of Et_2O, and then with 30 mL of pentane. This left an orange solid, which was dried in vacuo to give 2.17 g (95%, based on dmbpy) of pure desired product. ^{1}H NMR (C_6D_6) δ: dmbpy, 9.04(d, J = 6 Hz, 2H, arom), 6.98(s, 2H, arom), 6.46(d, J = 6 Hz, 2H, arom), 1.74(s, 6H, CH_3); DMSC, 7.70(d, J = 13 Hz, 1H, calix-CH_2), 7.34(d, 2H, arom CH), 7.30(d, 2H, arom CH), 7.04(d, 2H, arom CH), 6.95-(d, 2H, arom, CH), 4.67(d, J = 15 Hz, 1H, calix-CH_2), 4.60(d, J = 16 Hz, 2H, calix-CH_2), 4.26(d, J = 16 Hz, 2H, calix-CH_2), 3.50(d, J = 13 Hz, 1H, calix-CH_2), 3.40(d, J = 15 Hz, 1H, calix-CH_2), 1.39(s, 18H, t-Bu), 1.03(s, 18H, t-Bu), 0.35(s, 3H, exo-SiMe), −1.05(endo-SiMe).

Reductive Coupling of Terminal Alkynes with Ketones Mediated by 1. [(DMSC)Ti(Me_3SiCCH)(*endo,exo*-Tol_2CO)$_2$] (20). [(DMSC)Ti{$C_6H_3(SiMe_3)_3$}] (**1**) (0.261 g, 0.250 mmol) was added to 10 mL of a pentane solution containing Tol_2CO (0.105 g, 0.500 mmol) and $Me_3SiC{\equiv}CH$ (0.25 mL, 1.75 mmol). This solution was allowed to stir for 6 h at ambient temperature, after which the volatiles were removed in vacuo. The residue was washed with ca. 3 mL of cold pentane and then recrystallized from ether. The yellow precipitate was dried in vacuo to give 0.23 g (72%) of product. Anal. Calcd for $C_{81}H_{96}O_6Si_2Ti$: C, 76.21; H, 7.31. Found: C, 76.53; H, 7.92. ^{1}H NMR (C_6D_6) δ: 7.30−7.40(m, 9H), 7.16(d, J = 8 Hz, 4H, *p*-Tolyl), 7.04(d, J = 8 Hz, 4H, *p*-Tolyl), 6.88−6.92(two AB doublets, J = 2 Hz, 4H), 6.84(d, J = 8 Hz, 4H, *p*-Tolyl), 4.62-(d, J = 14 Hz, 1 H), 4.12(d AB, J = 17 Hz, 2H), 3.98(d, J = 14 Hz, 1 H), 3.95(d AB, J = 17 Hz, 2H), 3.73(d, J = 14 Hz, 1 H), 2.70(d, J = 14 Hz, 1 H), 2.22(s, 3H, MeC_6H_4), 2.05(s, 3H, MeC_6H_4), 1.31(s, 18H, t-Bu), 1.23(s, 18H, t-Bu), 0.24(s, 3H, exo-SiMe), 0.06(s, 9H, $SiMe_3$), −1.42(s, 3H, endo-SiMe). ^{13}C NMR (C_6D_6) δ: 159.1(TiOC), 153.3, 150.0, 148.5, 148.0, 143.5, 143.4, 142.7, 136.9, 135.1, 133.7(br), 130.1, 128.9(br), 128.3, 126.4-(br), 125.6, 124.8, 93.8($C(MeC_6H_4)_2$), 86.6($C(MeC_6H_4)_2$), 39.7-(calix-CH_2), 37.9(calix-CH_2), 35.5(calix-CH_2), 34.0 ($C(CH_3)_3$), 33.9 ($C(CH_3)_3$), 31.7(br, $C(CH_3)_3$), 20.95(MeC_6H_4), 20.88-(MeC_6H_4), 2.2(exo-SiMe), −1.8(endo-SiMe).

A sample of **20** prepared in situ was decomposed with H_2O in ether. The suspension was allowed to stand for 15 min, then the insolubles were filtered off, and the filtrate was analyzed by GC−MS. $(CH_2)_5C(OH)C(Tol){=}CHC(OH)(CH_2)_5$ was the only species observed besides $C_6H_3(SiMe_3)_3$. EI-GC−MS: 446($M^+ - H_2O$), 431($M^+ - H_2O, - CH_3$), 369($M^+ - H_2O, - Ph$), 341($M^+ - H_2O, - PhCO$), 292($M^+ - H_2O, - 2Ph$), 135($M^+ - 329$), 105-($PhCO^+$), 73(Me_3Si^+).

[(DMSC)Ti(Me_3SiCCH)(*endo,exo*-Ph_2CO)$_2$] (21). A 0.020 mmol sample of **1** was added to a 0.6 mL C_6D_6 solution containing 0.040 mmol of Ph_2CO and 0.100 mmol of $Me_3SiC{\equiv}$CH. The quantitative formation of **21** (22 °C) was followed by ^{1}H NMR. It was essentially complete in 3 h. The aromatic region was too complex to resolve; the metallacycle CH signal is likely buried under aromatic signals. ^{1}H NMR (C_6D_6) δ: 6.90−7.40(several multiplets, arom signals), 4.62(d, J = 14 Hz, 1 H), 4.11(d AB, J = 17 Hz, 2H), 3.98(d, J = 14 Hz, 1 H), 3.95-(d AB, J = 17 Hz, 2H), 3.72(d, J = 14 Hz, 1 H), 2.69(d, J = 14 Hz, 1 H), 1.31(s, 18 H, t-Bu), 1.18(s, 18 H, t-Bu), 0.26(s, 3 H, exo-SiMe), 0.02(s, 9H, $SiMe_3$), −1.38(s, 3 H, endo-SiMe).

[(DMSC)Ti(TolCCH)(*endo,exo*-$C_6H_{10}O$)$_2$] (22). [(DMSC)-Ti{$C_6H_3(SiMe_3)_3$}] (**1**) (0.366 g, 0.350 mmol) was added to a 4 mL pentane solution containing Tol$C{\equiv}$CH (0.089 mL, 0.70 mmol) and cyclohexanone (0.071 mL, 0.70 mmol). This mixture was stirred for 2 min at ambient temperature, then was allowed to stand for 2 h. A yellow precipitate began to separate, and the reaction mixture was cooled to −15 °C for 24 h. After that the supernatant was decanted and the microcrystalline residue washed with cold pentane and dried in vacuo to give 0.190 g (45%) of yellow product as a bis(pentane) adduct. Anal. Calcd for $(C_{67}H_{86}O_6SiTi)(C_5H_{12})_2$: C, 76.58; H, 9.18. Found: C, 76.59; H, 9.18. ^{1}H NMR (C_6D_6) δ: 7.29(d, J = 2 Hz, 2H), 7.26-(d, J = 2 Hz, 2H), 7.15(d, J = 8 Hz, 2H, tolyl), 7.14(d, J = 2 Hz, 2H), 7.06(d, J = 2 Hz, 2H), 6.98(d, J = 8 Hz, 2H, tolyl), 6.05(s, 1H, HC=C), 4.63(d, 1H, J = 14.5 Hz, calix-CH_2), 4.46-(d, 1H, J = 15 Hz, calix-CH_2), 4.24(d, 2H, J = 17 Hz, calix-CH_2), 4.04(d, 2H, J = 17 Hz, calix-CH_2), 3.60(d, 1H, J = 14.5 Hz, calix-CH_2), 3.55(d, 1H, J = 15 Hz, calix-CH_2), 2.14(s, 3H, $C_6H_4CH_3$), 1.3−2.0(several multiplets, 20H, cyclohexyl rings), 1.41(s, 18H, t-Bu), 1.34(s, 18H, t-Bu), 0.15(s, 3H, exo-SiMe), −1.37(s, 3H, endo-SiMe). ^{13}C NMR (C_6D_6) δ: 159.3(TiOC), 150.9, 150.3, 143.6, 143.4, 142.9, 137.0, 136.1, 132.5, 130.1, 129.3, 129.0, 128.5, 127.2, 127.0, 126.5, 126.2, 125.2, 87.6-(cyclohexyl CO−Ti), 83.2(cyclohexyl CO−Ti), 40.5, 39.6, 37.8, 38.0(1C, calix-CH_2), 35.3(1C, calix-CH_2), 34.3($C(CH_3)_3$), 34.1-($C(CH_3)_3$), 31.9($C(CH_3)_3$), 31.7($C(CH_3)_3$), 25.4(cyclohexyl ring CH_2), 25.3(cyclohexyl ring CH_2), 23.5(cyclohexyl ring CH_2), 21.7(cyclohexyl ring CH_2), 20.9($C_6H_4CH_3$), 2.1(exo-SiMe), −3.1-(endo-SiMe).

A sample of **22** was decomposed with H_2O in ether. The suspension was allowed to stand for 15 min, then the insolubles were filtered off, and the filtrate was analyzed by GC−MS. $(CH_2)_5C(OH)C(Tol){=}CHC(OH)(CH_2)_5$ was the only species observed. EI-GC−MS: 296($M^+ - H_2O$), 253($M^+ - H_2O, - C_3H_7$), 225($M^+ - 89$), 197($M^+ - H_2O, - C_6H_{11}O$), 185($M^+ - 129$).

[(DMSC)Ti($HCCCH_2OMe$)(*endo,exo*-$C_6H_{10}O$)$_2$] (23). [(DMSC)Ti{$C_6H_3(SiMe_3)_3$}] (**1**) (0.209 g, 0.200 mmol) was added

to a 4 mL pentane solution containing $HC{\equiv}CCH_2OMe$ (0.025 mL, 0.60 mmol) and cyclohexanone (0.022 mL, 0.22 mmol). This mixture was stirred for 2 min at ambient temperature, then was allowed to stand for 1 h. A pale-yellow precipitate began to separate, and the reaction mixture was cooled to −15 °C for 24 h. After that the supernatant was decanted and the residue washed with cold pentane and dried in vacuo to give 0.091 g (45% based on Ti) of pale-yellow product. Anal. Calcd for ($C_{62}H_{84}O_7SiTi$): C, 73.20; H, 8.32. Found: C, 73.41; H, 8.68. ^{1}H NMR (C_6D_6) δ: 7.29(br, 2H), 7.20(br, 2H), 7.16(br, 2H), 7.05-(br, 2H), 5.83(br s, 1H, HC═C), 4.63(br d, 1H, J = 14 Hz, calix-CH_2), 4.44(br d, 1H, J = 14 Hz, calix-CH_2), 4.17(br d, 2H, J = 17 Hz, calix-CH_2), 4.01(br d, 2H, J = 17 Hz, calix-CH_2), 3.74(br s, 2H, CH_2OCH_3), 3.63(br d, 1H, J = 14 Hz, calix-CH_2), 3.57-(br d, 1H, J = 14 Hz, calix-CH_2), 3.10(sharp s, 3H, CH_2OCH_3), 1.3−2.0(several multiplets, 20H, cyclohexyl rings), 1.41(br s, 18H, t-Bu), 1.34(br s, 18H, t-Bu), 0.12(br s, 3H, exo-SiMe), −1.37(br s, 3H, endo-SiMe).

A sample of **23** was decomposed with H_2O in ether. The suspension was allowed to stand for 15 min, then the insolubles were filtered off, and the filtrate was analyzed by GC−MS. $(CH_2)_5C(OH)C(CH_2OCH_3){=}CHC(OH)(CH_2)_5$ was the only species observed. EI-GC−MS: 250($M^+ - H_2O$).

[(DMSC)Ti(HCCCH$_2$NMe$_2$)(*endo*,*exo*-C$_6$H$_{10}$O)$_2$] (24). [(DMSC)Ti{$C_6H_3(SiMe_3)_3$}] (**1**) (0.209 g, 0.200 mmol) was added to a 4 mL pentane solution containing $HC{\equiv}CCH_2NMe_2$ (0.050 mL, 0.46 mmol) and cyclohexanone (0.040 mL, 0.40 mmol). This mixture was stirred for 2 min at ambient temperature, then was allowed to stand for 1 h. The volatiles were removed in vacuo, and the residue was washed with pentane and dried in vacuo to give 0.135 g (65%) of pale-yellow product. ^{1}H NMR (C_6D_6) δ: 7.30(br, 2H), 7.22(br, 2H), 7.16(br, 2H), 7.06(br, 2H), 5.83(br s, 1H, HC═C), 4.64(br d, 1H, J = 14 Hz, calix-CH_2), 4.45(br d, 1H, J = 15 Hz, calix-CH_2), 4.18(br d, 2H, J = 17 Hz, calix-CH_2), 4.02(br d, 2H, J = 17 Hz, calix-CH_2), 3.64(br d, 1H, J = 15 Hz, calix-CH_2), 3.57(br d, 1H, J = 14 Hz, calix-CH_2), 2.73(br s, 2H, CH_2NMe_2), 3.10(sharp s, 6H, $CH_2N(CH_3)_2$), 1.3−2.0(several multiplets, 20H, cyclohexyl rings), 1.42(br s, 18H, t-Bu), 1.35(br s, 18H, t-Bu), 0.14(br s, 3H, exo-SiMe), −1.35(br s, 3H, endo-SiMe). ^{1}H NMR in toluene-d_8 is essentially identical; cooling of the C_7D_8 solution below 0 °C causes the ^{1}H NMR peaks to sharpen, staying at approximately the same chemical shift. ^{1}H NMR spectra obtained at temperatures in the 25−100 °C range show progressive broadening of the peaks, with the increase of temperature resulting in an essentially featureless spectrum at 100 °C with a single broad t-Bu resonance.

A sample of **24** was decomposed with H_2O in ether. The suspension was allowed to stand for 15 min, then the insolubles were filtered off, and the filtrate was analyzed by GC−MS. $(CH_2)_5C(OH)C(CH_2NMe_2){=}CHC(OH)(CH_2)_5$ was the only species observed. EI-GC−MS: 261($M^+ - H_2O$).

[(DMSC)Ti(HCCCH$_2$OSiMe$_3$)(*endo*,*exo*-C$_6$H$_{10}$O)$_2$] (25). [(DMSC)Ti{$C_6H_3(SiMe_3)_3$}] (**1**) (0.021 g, 0.020 mmol) was added to a 0.6 mL C_6D_6 solution containing $HC{\equiv}CCH_2OSiMe_3$ (0.008 mL, 0.050 mmol) and cyclohexanone (0.004 mL, 0.040 mmol). This mixture was shaken for 2 min at ambient temperature, then was allowed to stand for 15 min. The presence of the title compound was revealed by ^{1}H NMR. The peaks were very broad, and full assignment was impossible; however key signals could be identified and the overall similarity to the spectra of **22**−**24** was evident. Selected ^{1}H NMR signals δ: 7.0−7.18(3 br multiplets overlapping with C_6D_5H peak, 8H), 5.96(br s, 1H), 4.35−4.70(2 br doublets, 2H), 3.8−4.25(br peaks, overlapping with CH_2 of the excess alkyne), 3.50−3.75-(2 br doublets, 2H), 1.2−2.0(br cyclohexyl resonances), 1.42 and 1.34 (2 br singlets, calixarene t-Bu), −1.37(br s, 3H, endo-SiMe), exo-SiMe and the $SiMe_3$ peak of the product are obscured by the peaks of $HC{\equiv}CCH_2OSiMe_3$ and its cyclotrimerization products.

A sample of **25** was decomposed with H_2O in ether. The suspension was allowed to stand for 15 min, then the insolubles were filtered off, and the filtrate was analyzed by GC−MS. $(CH_2)_5C(OH)C(CH_2OSiMe_3){=}CHC(OH)(CH_2)_5$ was observed. EI-GC−MS: 306($M^+ - H_2O$).

X-ray Crystal Structure Determination of Complexes 7 and 20. Single crystals suitable for an X-ray diffraction study were obtained for **7** by slow reaction of $Bu^tC{\equiv}CH$ with **1** in pentane in the presence of bipyridine, and for **20** by recrystallization from ether solution at −15 °C. Crystals of **20** grew as twins; hence the crystal used for the X-ray diffraction study was cut from a larger twinned crystal. Each crystal was coated with Paratone-N prior to mounting on the diffractometer. Data collection was performed at 173 K on a Nonius Kappa CCD diffractometer. The poor quality of the crystal of **7** did not allow for satisfactory refinement. For **20**, a transformation of the data frames to undistorted projections of the reciprocal lattice showed that a small volume of the second individual was still present. The precision of the data was limited by the presence of the diffraction pattern from this second individual. The *tert*-butyl groups including atoms C29 and C41 are disordered with occupancy factors of 0.877(6) and 0.643(9) for the major component. Restraints were applied to the 1,2 and 1,3 distances of these two groups and of the two ether molecules, one of which is located on a 2-fold axis. The H atoms attached to atoms C30B−C32B (occupancy 0.123) were not included in the model, and these C atoms were refined isotropically.

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Supporting Information Available: A summary of crystallographic parameters, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **7** and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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